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Synthesis and study of structure of the iron chloride – polyvinylpyrrolidone complex

The polymer-metal complex on the basis of iron (III) chloride and a polyvinylpyrrolidone (PVP) was synthesized. The composition of this complex was established by potentiometric and conductometric methods. Titration curves were constructed and the optimum molar ratio of the reacting components was found ($k = [Fe^{3+}]/[PVP] = 0.24$). The obtained experimental data confirm formation of a polymeric complex of iron where one metal ion is bonded with four compound monolinks of a polyvinylpyrrolidone. Coordination saturation of metal ion in this complex is realized due to the molecules of solvent or anions of iron salt. On the basis of the modified Bjerrum's method constants of stability of a polymeric complex at various values of ionic strength of solution were calculated on which thermodynamic equilibrium constants of the studied processes were found. On the basis of thermodynamic constants of stability, using isotherm equations and isobars of Vant Hoff and Gibbs, changes of Gibbs' energy ($\Delta_r G^0$), enthalpy ($\Delta_r H^0$) and entropy ($\Delta_r S^0$) were calculated. Complexing reactions of iron ions with polyvinylpyrrolidone are accompanied by exo-effects what point to the negative values of an enthalpy change during reaction. The negative values of an entropy change ΔS at the negative change of an enthalpy ΔH indicated that the studied reaction is possible at rather low temperatures. It was established that oxygen atoms of polymeric ligands were involved in formation of a coordination bond with a metal ion. It was established that oxygen atoms of polymeric ligands took part in formation of a coordination bond with a metal ion. Using IR-spectroscopy and scanning electron microscopy a structure and morphology of the synthesized complex iron (III)chloride-polyvinylpyrrolidone were investigated. Results of electron microscopy indicate on formation of polymeric films of a complex with cellular nonuniform amorphous structure.

Keywords: polyvinylpyrrolidone, iron, complexing, Bjerrum's method, constant, stability, composition, thermodynamics.

Introduction

Iron (III) complexes are widely used as catalysts of many organic processes, because of the features of an electronic structure of iron in oxidized (d^5) and reduced (d^6) states, a possibility of regeneration by oxygen, high complexing ability and good solubility in organic solvents. Owing to interaction metal-ligand homogeneous catalysts on the basis of iron chloride ($FeCl_3$) have a high activity and selectivity in Michael reaction [1], allylation of aldehydes with allyltrimethylsilane [2], acetal-ene reaction [3], conversion of epoxides to acetonides [4], oxidative coupling reaction of 1,2-diarylethylene derivatives [5], synthesis of coumarins from phenols and β-ketoesters [6]. In turn, poly(N-vinyl-2-pyrrolidone) (PVP) is nontoxical, water-soluble and biologically compatible and therefore ecologically harmless polymeric ligand [7, 8]. It is stable against thermal degradation in solution and in relation to acids and salts. Due to ability to complexation, application of PVP as a ligand allows to obtain stable complexes with the transitional metals [9, 10]. In literature there are not numerous data on use of catalysts on the basis of iron (III) complexes with polymers and various branched ligands in oxidizing reactions [11–13]. It should be noted that according to literary and pa-